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Granting Date: October 28, 2000

Title: Ring-opening polymerization phenolic resins and fiber reinforced composites

Abstracts:

The invention is related to a fiber reinforced ring-opening polymerization phenolic resins composites. It was manufactured by blending self made benzoxazine, epoxy resin and/or phenolic resin, changing the category and dosage of solvent, catalyst or harder, then immersing fiber or fabric. This product has good thermal stability and excellent electrical, physical and mechanical properties, especially high temperature mechanical properties, and is suitable to be used as heat-resistant structure materials and electrical insulating materials servicing at 150-180°C for long time. The advantages of the invention composites are low cost, and easy commercialization and industrial application, having outstanding economic and society effect.

Claims:

1 A fiber reinforced ring-opening polymerization phenolic resins composites, whose character lies in that the formula ingredients of matrix resin (share in weight) as following:

Benzoxazine	30~90
Epoxy resin	10~50
Phenolic resin	20~70
Harder or catalyst	0.1~8
Solvent	80~120

According to above formula, each ingredient being weighted respectively and mixed together for preparing gel solution. The viscosity of this gel solution is (coating Number 4 cup at 25°C) 10 ~ 20 seconds. The gel transition time is 0.5~6 minutes (plate knife method at 150°C). The solid content of gel solution is 40~60%. Fiber or cloth, chosen from glass fiber, glass cloth, carbon fiber and carbon cloth, is impregnated in gel solution. The heating condition for gel solution is: 5-15minutes at 50-140°C. The volatile content in the resultant impregnated composites is < 2%, the solvent resin content is >90%, the gel content is 35~45%. The compression molding temperature for composites is 160~200°C and compression curing time is 2~3 hours.

2 Fiber reinforced ring-opening polymerization phenolic resins composites of claim1, which is characterized in that the formula ingredients of raw materials for benzoxazine (share in weight) are as following:

Phenol compound	30~70
Amine compound	30~70
Formaldehyde or paraformaldehyde	25~35
Solvent	120~250

The synthesis of benzoxazine ring structure comprises two steps. First, amine compound and formaldehyde or paraformaldehyde react in solvent to produce N-dihydroxymethyl compound though controlling the PH value between 8~10, keeping N-dihydroxymethyl compound stable in the solution; Second, phenol compound is added, N-dihydroxymethyl compound first reacts on the ortho position of phenolic hydroxy group, then phenolic hydroxy dehydrates and ring closes to produce benzoxazine ring structure compound. The ring formation ratio is 60~90%. Or phenol compound is quickly added into amine in formaldehyde solution at 40~60°C to produce benzoxazine ring structure compound.

3 Fiber reinforced ring-opening polymerization phenolic resins

composites of claim1 or Claim 2, which is characterized in that the phenol compound used for preparing benzoxazine used in composites is selected from phenol, *p*-cresol, *p*-tert-butylphenol, *m*-cresol, *p*-chlorophenol, *p*-nitrophenol, *p*-cyanophenol, biphenol-A, biphenol-S, dihydroxydiphenylate, *p*-phenyldiphenol or low molecular weight novolac resin.

4 Fiber reinforced ring-opening polymerization phenolic resins composites of claim1 or claim2, which is characterized in that the amine compound used for preparing benzoxazine used in composites is selected from methyleamine, aniline, ammonia, diphenyleneamine, *m*-phenyleneamine, hexanediamine, ethylenediamine, di-phenylate diamine or diphenylsulfone diamine.

5 Fiber reinforced ring-opening polymerization phenolic resins composites of claim1 or claim2, whose character lies in that the solvent used for preparing benzoxazine and composites is selected from toluene, dimethylbenzene, dioxane, ethanol, dichloromethane, isopropanol or tetrahydrofuran.

6 Fiber reinforced ring-opening polymerization phenolic resins

composites of claim1, which is characterized in that the harder or catalyst for resin system is selected from inorganic acid, organic acid, primary amine, second amine, tertiary amine, acid anhydride or methenamine.

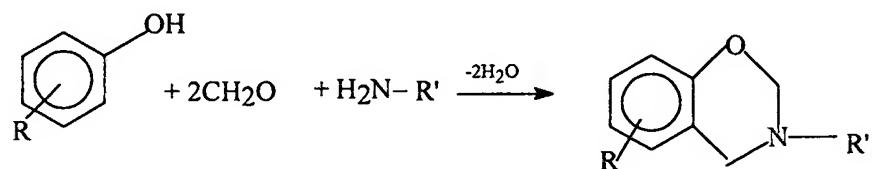
7 Fiber reinforced ring-opening polymerization phenolic resins composites of claim2, which is characterized in that the alkaline compound for controlling the PH value is selected from KOH, NaOH, Mg (OH)₂, triethanolamine, triethylamine, pyridine or imidazole.

Description

Title: Ring-opening polymerization phenolic resins and fiber reinforced composites

The invention relates to a fiber reinforced ring-opening polymerization phenolic resins composites and their manufacturing method. This kind of resins contain benzoxazine (1-oxane-3-zaletetrahydronaphthalene) cyclic structure compound (one molecular at least containing one cyclic structure), epoxy resin and/or phenolic resin, harder and/or catalyst. This kind of fiber reinforced composites can be used as heat-resistant structure materials and electrical insulating materials.

In 1940th, foreign researchers studied the synthesizing reaction of phenol compound, amine compound formaldehyde systematically. The compound which contain benzoxazine ring was synthesized, the reaction equation is:



Where R = hydrogen, halogen, alkyl, alkoxy etc.

R'= aliphatic group or aromatic group

Compared with other phenolic condensing reaction, the outstanding character of this reaction is that phenol participates in ring closing reaction.

In 1973, German H.Schreiber disclosed the ring-opening polymerization reaction of benzoxazine in DE2255504 and DE2323936. Novel phenolic plastics can be obtained by copolymerization of benzoxazine compound and epoxy resin or phenolic resins. The heat resistant property of this ring-opening polymerization phenolic resin product is low. Although it is treated at 200°C for 21hours, the Martin temperature is also below 100°C. Schreiber had tried a lot, but the highest Martin temperature is only 120-130°C. At last, plastic product whose glass transition temperature is above 200°C was obtained by copolymerization of alicyclic epoxy resin and benzoxazine compound. This technique was awarded patent US32745, at the Sep. 6th, 1998. Because the cost of alicyclic epoxy resin is high, it is difficult for this product to realize industrialized production and application. At the same time, American Higginbottom was granted patent US4557979 about mixing benzoxazine compound and amine for producing cataphoretic coating.

The objective of this invention is to provide one kind of fiber

reinforced ring opening polymerization phenolic resin composites for overcoming the shortcomings of existed techniques. This kind of composites is prepared by blending self-made benzoxazine and epoxy resin and/or phenolic resin, changing the category and dosage of solvent, catalyst or harder, then immersing fiber or fabric. This product has good thermal stability and excellent electrical, physical and mechanical properties and can be used as heat-resistant structure materials and electrical insulating materials servicing at 150-180°C for long time.

The formula ingredients of fiber reinforced ring opening polymerization phenolic resins composites of the invention are (share in weight):

Benzoxazine	30~90
Epoxy resin (general or high property epoxy resin chosen from bifunctional, trifunctional, tetrafunctional epoxy resin)	10~50
Phenolic resin (novolac phenolic with different molecular weight)	20~70
Harder or catalyst (inorganic acid, organic acid, primary amine, second amine, tertiary amine, acid anhydride or methenamine)	0.1~8

Solvent (toluene, dimethyl benzene, ethanol, acetone or tetrahydrofuran)

80~120

According to above formula, each ingredient is weighted respectively and mixed together for preparing gel solution. The viscosity of this gel solution is (coating Number 4 cup at 25°C) 10 ~ 20 seconds. The gel transition time is 0.5~6 minutes (plate knife method at 150°C). The solid content of gel solution is 40~60%. Fiber or cloth, selected from glass fiber, glass cloth, carbon fiber and carbon cloth, is impregnated in gel solution. For completely removing solvent and properly increasing the conversion of precursor in order to meet the need for press molding process of composites, based on the research results of cure behavior and gel transition time of resin by using DTA and TGA, the heating condition for gel solution is set as following: 5-15minutes at 50-140°C. The volatile content in the resultant impregnated composites is < 2%, the solvent resin content is >90%, the gel content is 35~45%. The final compression molding temperature for composites is 160~200°C and compression curing time is 2~3 hours. Various composites products can be obtained.

Benzoxazine precursor is synthesized by using phenol compound,

amine compound and formaldehyde. The formula ingredients for raw materials is (share in weight):

Phenol compound (phenol, *p*-cresol, *p*-tert-butylphenol, *m*-cresol, *p*-chlorophenol, *p*-nitrophenol, *p*-cyanophenol or low molecular weight novolac resin) 30-70

Amine compound(methyleamine , aniline, ammonia, diphenylmethyldiamine , *m*-phenyleneamine, di-phenylate diamine, diphenylsulfone diamine, hexanediamine or ethylenediamine) 30-70

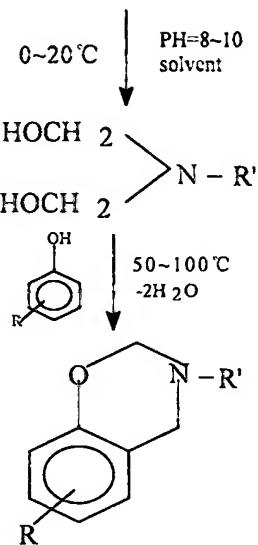
Formaldehyde or paraformaldehyde

25-35

Solvent(toluene, dimethylbenzene, dioxane, ethanol, dichloromethane, isopropanol or THF)

120-250

The reaction formula of benzoxazine is as following:



R = hydrogen, halogen, alkyl, alkoxy etc.

R' = aliphatic group or aromatic group

The synthesis of benzoxazine ring structure comprises two steps.

First, amine and formaldehyde or paraformaldehyde react in solvent to produce N-dihydroxymethyl compound though controlling the PH value between 8~10 by adding KOH, NaOH, $\text{Mg}(\text{OH})_2$, triethanolamine, triethylamine, pyridine or imidazole , keeping N-didydroxymethyl compound stable in the solution and thus preventing it from etherifying or intramolecular dehydrating to produce Schiffs base; second, phenol compound is added, N-didydroxymethyl compound first reacts on the ortho position of phenolic hydroxy group, then phenolic hydroxy dehydrates and ring closes to produce benzoxazine ring structure

compound. The ring formation ratio is 60~90%.

The benzoxazine ring structure compound can also be synthesized when phenol compound is quickly added into amine in formaldehyde solution at higher temperature(40~60℃).

In table 1, the properties of ring open polymerization phenolic resin matrix glass cloth laminate was compared with those of several main H Grade electrical insulating glass cloth laminates (including modified phenyl ether resin matrix glass cloth laminate, organic silane epoxy resin matrix glass cloth laminate and bismaleimides matrix glass cloth laminate). The mechanical and electrical properties of ring open polymerization phenolic resin matrix glass cloth laminate attain or exceed those of above other laminates except that Matin temperature is 222℃, a little lower than that of others. Especially, the flexural strength of the invention laminate at 180℃ is 262Mpa, the retention rate >50%. Fiber reinforced ring open polymerization phenolic resin composites are suitable to be used as heat resistant machinery and structure parts, heat resistant lamina of vacuum pump and can service at 150~180℃ for long time. And they are also suitable to be used in equipment, such as F, H grade electric motor and transformer etc. as heat resistant component, eg. slot, insulating gasket, gasket and junction plate etc..

This invention has several advantages as following:

1 Ring open polymerization phenolic resin is one kind of new developed resin, no volatages evolving during curing, overcoming the disadvantages of traditional phenolic resins, such as evolution of volatages and the hole content rate of product is low. Fiber reinforced composites can be easily processed by using ordinary instruments and easily realized industrial production.

2 The thermal stability of ring opening polymerization phenolic resin is high. The electrical and mechanical properties of fiber reinforced composites are excellent, especially high temperature mechanical properties. It is suitable for composites to be used as heat resistant and high property structure materials and electrical insulating materials.

3 The synthesis of the invention benzoxazine is simple, easily processed by using ordinary equipment. The ring formation ratio is high.

4 The cost of ring opening polymerization phenolic resin is greatly lower than that of bismaleimides resins, phenyl ester resins and organic silane resins. The invention resin has high property price rate and outstanding economic efficiency.

Example:

1 Benzoxazine solution in toluene (40% solid content)synthesized in example 5, 200shares in weight; epoxy resin(6106),20shares in weight; and N,N-dimethylbenzylamine, 1share in weight were charged into the flask equipped with stirrer, reflux condenser and thermometer, then were mixed at 50°C for 30mintues. Ring opening polymerization phenolic resin solution (43% solid content), whose viscosity and gel time were 12.5seconds(coating 4# cup at 25°C) and 4 minutes (plate knife method, at 150°C) respectively was obtained. E-glass cloth treated by KH-550 was impregnated in resin solution. The prepgs was obtained after heating at 100~120°C for 12minutes. 21 layers of prepgs were superposed together and put in the mold of pressing machine. Open the heater and put pressure according to gel flow condition, put full pressure at 150~160°C, cured at 170~180°C for 2 hours and postcured at 170°C for 3 hours, the red brown glass cloth laminate was obtained. The temperature of lost weight of 5%, 15% and 50% was 336°C, 468°C and 609°C respectively by TGA analyzing. The water absorption rate of laminate (immersed in distilled water for 48hours) was 0.7%. The adhesion strength of laminate was 6.7KN. The flexural strength of laminate at normal temperature and 180°C were 517Mpa, 267Mpa respectively. The electric volume resistivity at normal temperature and 180°C of laminate were $4.1 \times 10^5 \text{ M}\Omega \cdot \text{m}$ and

$5.2 \times 10^2 \text{ M}\Omega \cdot \text{m}$ respectively, normal dielectric constant and dielectric loss factor of laminate are 4.75 and 0.03 respectively.

2 Benzoxazine solution (32%solid content) synthesized in example 4, 250 shares in weight; epoxy resin,20shares in weight; and N,N-dimethylbenzylamine, 1 share in weight were charged into the flask equipped with stirrer, reflux condenser and thermometer, and then were mixed at 50°C for 30mintues, orange ring opening polymerization phenolic resin solution, whose viscosity and gel time were 11.5seconds(coating 4# cup at 25°C) and 5.67 minutes(plate knife method, at 150°C) respectively, was obtained. E-glass cloth treated by KH-550 was impregnated in resin solution. The weak red glass cloth laminate was obtained according to molding process described in example 1. The flexural strength of laminate at normal temperature and 180°C were 650Mpa and 223Mpa respectively. the electric volume resistivity of it was $4.2 \times 10^6 \text{ M}\Omega \cdot \text{m}$.

3 The benzoxazine solution synthesized in example 5 was distilled under lower pressure for removing solvent. The solid benzoxazine, 50 shares in weight; novolac resin, 50 shares in weight; methenamine, 6 shares in weight were dissolved in acetone, 100 shares in weight and stirred at 30°C for 30 minutes. The red brown ring opening polymerization phenolic resin solution was obtained. The viscosity and gel time of

solution were 14 seconds(coating 4# cup at 25°C) and 37 seconds (plate knife method at 150°C) respectively. E-glass cloth treated by KH-550 was impregnated in resin solution. The prepgs was obtained after heating at 60°C for 10minutes. 22 layers of prepgs were superposed together and put in the mold of pressing machine at 90°C. Open the heater and add put pressure according to gel flow condition, put full pressure at 130°C, cured at 170°C for 2 hours under pressure and postcured at 170°C for 3 hours. The yellow brown glass cloth laminate was obtained. The temperature of lost weight of 5%, 15% and 50% for laminate were 295°C, 435°C and 530°C respectively by TGA analyzing. The flexural strength of laminate at normal temperature and 155°C were 576Mpa and 318Mpa respectively. The electric volume resistivity and dielectric constant of laminate were $4.1 \times 10^6 \text{M}\Omega \cdot \text{m}$ and 4.65.

4 Paraformaldehyde,12g(0.4mol); ethanol, 20ml; NaOH, 0.2g were charged into the flask equipped with stirrer, condenser and thermometer, reacted at 40°C for 1 hour till the solution became transparency(PH>8). The temperature of solution was declined to 5°C in ice bath. Anline, 18.8g(0.2mol) and dioxane,60ml were added in, stirred at 5°C for 1hour. Then biphenol-A, 22.8g (0.1mol) and dioxane, 40ml were added. The temperature of solution was increased to 80°C, refluxed for 5hours and

then declined. The light yellow transparent benzoxazine solution was obtained. The ring formation ratio was >80% checked by H-NMR.

5 Paraformaldehyde,6g(0.2mol); ethanol, 20ml; NaOH, 0.1g reacted at 40°C for 1 hour till the solution became transparency. The temperature of solution was declined to 14°C.Toluene, 20ml and diphenylmethanediamine,9.98g(0.05mol)were added, The solution was increased to 80°C, refluxed for 5hours and then be declined. Keep the solution till it was demixing. Water was separated out. The light yellow benzoxazine toluene solution was obtained. The ring formation ratio was >70%.

6 Formaldehyde (36 % aqueous solution),7.6ml(0.1mol), triethylamine,0.18g were charged in flask, stirred and increased the temperature to 50°C. Diphenylmethanediamine,4.95g (0.025mol) was added and when it dissolved, m-cresol,5.4g(0.05mol) and toluene 30ml were added. Increased the temperature to 80°C and refluxed for 4hours, declined the temperature. The white benzoxazine powder was obtained. The ring formation ratio was >95%.

The properties testing methods are explained as following:

1 The heat resistant Grade of laminate was tested according to JB2624-79 "Quickly aged experimental method for electrical insulating immersion coating and coating cloth---skive line property".

2 The mechanical and electrical properties of laminate were tested according to GB5130-85 "Electrical insulating laminate experimental method".

3 The viscosity of various kinds of resin solutions were tested by using Number 4 cup, according to GB1723-79 "The viscosity of coating testing method".

4 The solid content of resin solutions was tested according to GB1725-88 "the solid content of coating testing method".

5 The volatile of prepgs was tested according to GB6056-85 " The volatile of prepgs testing method".

6 The solvent resin content of prepgs was tested according to GB7192-87 " the resin content of prepgs testing method".

Table 1 The properties of several H Grade glass cloth laminates

Index	Value of index	3255 diphenyl ether matrix cloth laminate, Density(g/cm ²)	9334 bismaleimides glass matrix laminate, Heat resistant grade	3250 silane epoxy resin matrix glass cloth laminate, Martin temperature(℃)	MDAPFI-EGF organic cloth laminate of this invention
Flexura Strength h (Mpa)	Normal condition 180℃	≥343	≥343	≥250	1.73
Tensile strength in longitudinal direction (Mpa)			≥176	≥250	H
Impact strength in longitudinal direction (KJ/m ²)		≥294		≥147	H
Adhesion strength (N)		≥147		≥196	222
Electric surface resistivity (MΩ)	Normal condition After immersed in water	≥10 ⁵	≥10 ⁶	≥10 ⁷	1.7
Electric volume resistivity(MΩ* m)	Normal condition After immersed in water	≥10 ⁵	≥10 ⁴	≥10 ⁵	4.6×10 ⁶
180℃	≥10 ²	≥10 ²	≥10 ²	≥10 ²	1.7×10 ⁷
Dielectric loss factor		≤0.05	≤0.04	≤0.04	0.012